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AGING AND DEGRADATION OF POLYOLEFINS
II. GAMMA-INITIATED OXIDATIONS OF ATACTIC
POLYPROPYLENE

Christian Decker, et al

Stanford Research Institute

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Final Report

August 31, 1972

For the Period May 1, 1971 to August 31, 1972

Report No. 11 for Project 8012-1, *Aging and Degradation of Atactic Polypropylene*

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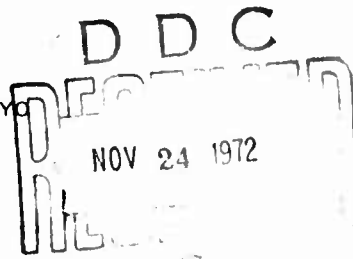
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CONTENTS

1.	OBJECTIVE.	1
2.	SUMMARY.	1
3.	BACKGROUND	3
4.	γ -INITIATED OXIDATIONS OF ATACTIC PP AT 22°	5
	4.1. Experimental Conditions and Analytical Methods.	5
	4.2. Rates and Products of Oxidations of PP at 22°	8
	4.3. Summary and Conclusions	16
5.	γ -INITIATED OXIDATIONS OF PP AT 45°	19
	5.1. Rates and Products of Oxidations of PP at 45°	19
	5.2. Comparison of PP Oxidations at 22° and 45°	26
	5.3. Comparison of DBPO- and γ -Initiated Oxidations of Atactic PP at 45°	27
6.	INHIBITED OXIDATIONS OF PP AT 45°	29
	6.1. Rates of Oxidations	29
	6.2. Caged and Free $\text{PO}_2\cdot$ Radicals.	33
	6.3. Calculation of k_a/k_p	35
	6.4. Changes in Molecular Weight	35
7.	OXIDATIONS OF PP IN HEXANE SOLUTION.	36
	7.1. γ -Initiated Oxidations of PP in Hexane at 45°	37
	7.2. DBPO-Initiated Oxidations of PP and Hexane.	41
8.	ACKNOWLEDGMENTS.	43

This report completely replaces, corrects, and extends Report No. 10 for Project 8012-1 and Report No. 8 for Project 8012-2. Section 7 is entirely new.

γ -INITIATED OXIDATIONS OF ATACTIC POLYPROPYLENE

1. OBJECTIVE

gamma → The study presents
The objective of this study is to determine the rates and products of oxidation of amorphous polypropylene (PP) as initiated by the action of γ rays, for comparison with the di-t-butylperoxy oxalate (DBPO)-initiated oxidations of PP¹ and with the γ -initiated oxidations of polyethylene and ethylene-propylene copolymers.² *gamma*

2. SUMMARY

Rates of oxygen absorption and oxidation products were determined in γ -initiated oxidations of atactic PP at 22° (Section 4). Data are given for four reaction times at each of five dose rates and correlated on the basis that the overall oxidation is the sum of two reactions that are first order and half order in rate of initiation (dose rate). The principal oxidation product is hydroperoxide (PO_2H), formed only by the half-order reaction. Radiation yields (G) for O_2 absorbed range from 9 to 63 depending on dose rate. One termination product, dialkyl peroxide (P_2O_2), results only from the first-order reaction. Total oxygen absorption and the minor products, alcohol (ROH) and carbonyl compounds (C=O), are associated with reactions of both orders. A correlating equation permits calculation of the products of oxidation

(1) E. Niki, C. Decker, and F. R. Mayo, Peroxide-Initiated Oxidations of Atactic Polypropylene, Final Report (No. 10) for SRI Project 8012-1 (August 1972).

(2) C. Decker, F. R. Mayo, and H. Richardson, Oxidations of Polyethylene and Ethylene-Propylene Copolymers, Final Report (No. 10) for SRI Project 8012-2 (August 1972).

at any rate of initiation at 22°, accounting for 100% of the oxygen absorbed in the first-order reaction and 89% of that absorbed in the half-order reaction. The origin of the alcohol and carbonyl compounds formed in the half-order reaction is discussed.

An increase in the temperature of irradiation to 45° leads to a threefold increase in oxygen absorption and in hydroperoxide formed; dialkyl peroxide and carbonyl compounds are hardly affected by the change in temperature (Section 5).

Oxidations carried out at 45° in the presence of 2,6-di-t-butyl-p-cresol show that this antioxidant scavenges only the polymer peroxy (PO_2^{\cdot}) radicals responsible for chain propagation outside the cage (Section 6). Thus, 84% of the PO_2^{\cdot} radicals disappear by geminate terminations in the cage, and only 16% escape from the cage to disappear by statistical terminations. Over the range of dose rates investigated, between 60 and 100 molecules of PO_2H are formed per initiating radical that escapes from the cage. The ratio of the rate constants for the reaction of PO_2^{\cdot} radicals with the antioxidant (k_a) and with the polymer (k_p) was determined to be $k_a/k_p = 4700 \pm 500$ in air.

Oxidations of PP, hexane, and their mixtures, with both γ and DBPO initiation, show that oxygen absorption by PP per initiating radical is about the same in bulk and in solution (Section 7). Hexane is much less reactive than PP in oxidation and has the net effect of an inert diluent, although its cooxidation may supply some faster-terminating radicals. In the transition from bulk to solution in oxidation of PP, the number of PO_2^{\cdot} radicals that escape the cage increases greatly, but their steady concentration decreases about a hundredfold. These results require a much higher termination constant in solution, partly offset by a propagation constant that is also higher.

3. BACKGROUND

Most of the work in this report was carried out by Dr. Christian Decker (cf. Section 8). The research on γ -initiated oxidations of PP is both a suitable extension of the work on DBPO-initiated oxidations of PP on one multisponsor project¹ and the foundation for the work on γ -initiated oxidations of polyethylene and ethylene-propylene copolymers on the related multisponsor project.² Since the work was carried out with very little cost to either group of sponsors, it is provided among the regular reports for each program.

In the absence of oxygen, γ -irradiation of PP leads to the formation of tertiary alkyl radicals and allyl radicals, identified by esr spectroscopy.³ The gases evolved consist of 99% hydrogen, the radiochemical yield of this gas ($G_{H_2} \sim 4.3$) being slightly higher than from high density polyethylene.⁴ Both crosslinking and main chain cleavage occur, with crosslinking only slightly exceeding cleavage.⁵

The γ -initiated oxidation of PP has been studied less intensively than that of polyethylene, and only a few kinetic data are available.⁶⁻⁹ The presence of peroxy radicals during γ oxidation of PP has been proved

-
- (3) H. Fisher and K. H. Hellwege, J. Polym. Sci., 56, 33 (1962).
 - (4) R. F. Hornbeck and W. W. Parkinson, ORNL 2413 (August 1957).
 - (5) R. M. Black and B. J. Lyons, Nature (London), 180, 1346 (1957).
 - (6) A. Chapiro, J. Polym. Sci., 34, 439 (1959); *ibid.*, 48, 109 (1960).
 - (7) A. Chapiro and T. Czvikovszky, J. Chim. Phys., 66, 1502 (1969).
 - (8) F. Kimura and I. Sakurada, Nippon Hoshasen Kobimski Kenkyu Kyokai Nemyo, 7, 33 (1966).
 - (9) P. Neudoerfl, Kolloid Z., Z. Polym., 224, 132 (1968).

by esr measurements.¹⁰⁻¹² An infrared study¹³ showed increasing concentrations of hydroxy groups and ketones with the irradiation time. The existence of a chain peroxydation at room temperature was proposed by Fisher et al.¹⁰ in their esr study of the γ -initiated oxidation of PP. This was suggested earlier by Chapiro⁶ and since confirmed⁷ in his study on the γ -peroxidation of PP. To differentiate hydroperoxide (PO_2H) and dialkyl peroxide (P_2O_2), Chapiro used the peroxidized polymer to initiate graft copolymerization. The thermal breakdown of a P_2O_2 leads to two $\text{PO}\cdot$ radicals, each of which in the presence of a monomer will give rise to one grafted branch, whereas homolysis of a PO_2H under similar conditions will give one grafted branch and one molecule of homopolymer (resulting from chain initiation by the $\text{OH}\cdot$ radical). When preirradiated in air, PP initiates graft copolymerization at room temperature but leads to the formation of considerable amounts of homopolymer, whereas polyethylene yields only small amounts of homopolymer. Chapiro and Czvikovszky⁷ suggested that the reason chain hydroperoxidation occurs at room temperature with PP but only above 60° for low molecular weight hydrocarbons¹⁴ is that the low mobility of the polymeric $\text{PO}_2\cdot$ radicals permits chain propagation because the termination reaction is so slow.

In the present work oxygen consumption and formation of oxidation products were followed during the γ -initiated oxidation of PP at 22° and 45° as a function of the irradiation time at different dose rates. Some

(10) H. Fisher, K. H. Hellwege, and P. Neudoerfl, J. Polym. Sci. A-1, 1, 2109 (1963).

(11) J. Chien and C. Boss, J. Amer. Chem. Soc., 89, 571 (1967).

(12) E. R. Klinshpont, V. K. Milinchuk, and S. Y. Pshezhetskii, Khim. Vys. Energ., 3, 357 (1969); Vysokomol. Soedin., B, 12, 88 (1970).

(13) S. Ohnishi, S. Sugimoto, and I. Nitta, J. Polym. Sci. A-1, 1, 625 (1963).

(14) N. A. Bakh, Radiat. Res., 1, 190 (Suppl. 1959).

inhibited oxidations in the presence of 2,6-di-t-butyl-p-cresol are also described.

4. γ -INITIATED OXIDATIONS OF ATACTIC PP AT 22°

4.1. Experimental Conditions and Analytical Methods

The polymers and procedures were like those used in Ref. 1. Atactic PP, supplied by Dr. H. M. Khelgatian of the Avisun Corporation, was purified and fractionated as follows: A pentane solution of polymer was washed with several solutions of 2% alcoholic KOH solution until the alcohol layer was no longer colored and then with 1 M aqueous HCl to remove stabilizer and any metals. For fractionation of this soluble PP, benzene and methanol were chosen as solvent and precipitant, respectively. The fraction used for this study had a number average molecular weight, calculated from intrinsic viscosity,¹⁵ of 14,300.

To obtain very thin layers of polymer, we prepared the samples as follows: PP was dissolved in a small quantity of pentane; Pyrex glass wool, about three times the weight of PP, was added to disperse the polymer. This glass wool was previously washed successively with acetone, hot aqueous N 10 NaOH, M/10 aqueous solution of ethylenediamine-tetraacetic acid and water, and finally dried in vacuo at room temperature. The solvent was then removed in vacuo from the frozen extract during three hours at room temperature. With this technique, very little polymer collects on the walls of the vessel, and the PP is randomly dispersed on the glass fibers, as can be seen by electron scanning microscopy. The thickness of the film was less than one micron, allowing fast diffusion of oxygen into the polymer.

(15) J. B. Kinsinger and R. E. Hughes, J. Phys. Chem., 63, 2002 (1959)

Sealed tubes containing the PP on glass wool and a known amount of pure oxygen, measured with a gauge at a pressure of 625 ± 0.2 mg Hg at $13-27^{\circ}$, were exposed to the γ rays of a cobalt source at dose rates between 470 and 1750 rad/min.

After oxidation, the remaining gas was removed from the frozen reactor (-196°C) and measured with a toepler pump. Removal of oxygen in a Cu-CuO furnace showed 0.4% of hydrogen after 70 hours of irradiation at 650 rad/min. The oxygen consumed is then the difference between the initial and final amounts of oxygen. Condensable products were then removed from the reactor at room temperature with the toepler pump. They represent about 5% by volume of ΔO_2 (Section 4.2). The oxidized polymer was recovered from the glass wool by extraction with benzene during two days at room temperature. The solution was filtered and the solvent then removed by freeze-drying. The polymer was dried in vacuo at room temperature during three days. The weight of PP recovered is 101% to 103% of the weight of the initial polymer, depending on the level of oxidation.

PO_2H was determined by iodometric titration of a benzene solution according to Hiatt's method.¹⁶ After 10 minutes reflux the peroxide content does not increase further with increasing refluxing time.

The total PO_2H and P_2O_2 in the oxidized PP were determined by the method III of Mair and Graupner¹⁷ according to the following procedure: Glacial acetic acid (25 ml) is refluxed for 15 minutes to reduce the blank. After cooling, 3 g NaI is dissolved and 5 ml of a xylene solution of oxidized PP (about 50 mg) is added to the mixture. One ml of 37% HCl is then added, and the mixture is immediately heated to boiling

(16) R. Hiatt and W.M.J. Strachan, J. Org. Chem., 28, 1894 (1963).

(17) R. D. Mair and A. J. Graupner, Anal. Chem., 36, 194 (1954).

under a reflux condenser. After 15 minutes refluxing, 50 ml of water is added through the condenser and the liberated iodine is titrated with an aqueous solution of 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$. This procedure is carried out under nitrogen to avoid the interference of oxygen from air. The nitrogen flow is cut off during heating of the flask contents, to avoid losses of I_2 , and resumed when heating stopped. The top of the condenser is closed with a valve to prevent air from diffusing to the refluxing mixture. Tests show that $\text{t-Bu}_2\text{O}_2$ is quantitatively reduced in only 5 minutes and liberates 1 mole of iodine per mole of peroxide. With the oxidized polymer, complete reduction is achieved in 15 minutes with no further liberation of iodine with increasing refluxing time. Blank experiments were run simultaneously with the original PP in a xylene solution; the blanks were about 10% of the determined peroxide ($\text{PO}_2\text{H} + \text{P}_2\text{O}_2$) contents.

Aldehydes and ketones were characterized by infrared spectroscopy (band at 1720/cm) using a 25% solution of PP in carbon disulfide. The extinction coefficient was measured using 2-octanone, 10-nonadecanone, and heptanal as model compounds.

The amount of POH was determined by infrared spectroscopy by subtracting from the absorption of the peak at 3380/cm the corresponding absorption of hydroperoxides, using t-amyl alcohol and $\text{t-AmO}_2\text{H}$ as model compounds. Figure 1 shows how the weak absorptions of these compounds at low concentrations, particularly of alcohol, make difficult the determination of alcohol by difference.

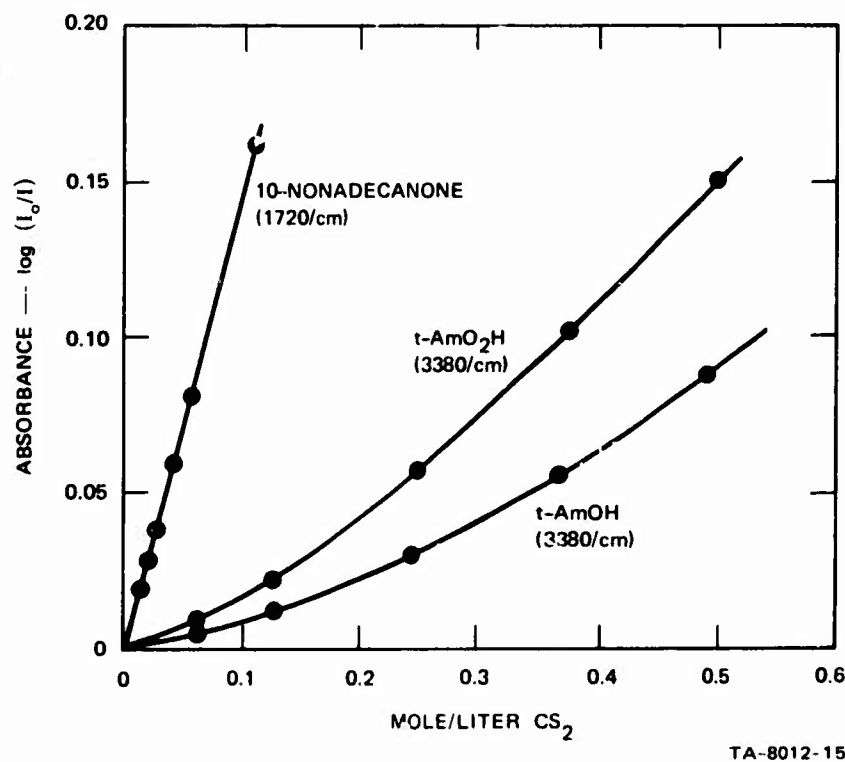
Molecular weights before and after oxidation were calculated from viscosities of benzene solutions at 35°C and from the relation:¹⁵

$$[\eta] = 2.7 \times 10^{-4} \bar{M}_n^{0.71}$$

assuming that all the polymers have normal molecular weight distributions. Intrinsic viscosities were calculated by one-point measurements using the Huggins equation in the form

$$[\eta] = \left[(1 + 4k'\eta_{sp})^{\frac{1}{2}} - 1 \right] / 2k'C$$

with $k' = 0.408$ and C in g/100 cc solvent.



TA-8012-15

FIGURE 1 CALIBRATION CURVES FOR IR ABSORPTIONS OF KETONE AND ALCOHOL GROUPS

4.2. Rates and Products of Oxidations of PP at 22°

We have investigated the oxidation of atactic PP at different times and dose rates at total doses between 1.3 Mrad and 11.6 Mrad. The oxygen uptakes and oxidation products observed in each experiment

(expressed in mole/kg PP) are shown in Table I. The main oxidation product is PO_2H , which accounts for more than 66% of the oxygen uptake, whereas POH , >C=O , and P_2O_2 account for about 7%, 10%, and 8%, respectively. Volatile oxidation products (H_2O , H_2O_2 , CO_2 , CH_2O) represent between 4% and 7% by volume of the amount of oxygen consumption and should account for about 4% of the missing oxygen in our material balance. As shown in Figures 2 and 3, the oxygen uptake at a given dose rate increases linearly with the irradiation time or total dose; over the whole range of doses investigated, the rate of oxidation is constant.

One of the major advantages of γ -initiated oxidations is that the rate of initiation is constant in a single experiment but can be easily varied in other experiments. To determine the kinetic orders of the reactions involved, we carried out oxidations of PP at four dose rates: 470, 650, 1050, and 1750 rad/min. Results are shown in Table II. When the rates of oxygen consumption and formation of oxidation products (R) are plotted as functions of the dose rate (I) on logarithmic scales, the relation obtained in Figure 4 has the form, $R = k I^x$, where the exponent x for each product is between 0.5 and 1. The formations of dialkyl peroxides and net chain scissions are first order in rate of initiation, but the rate of formation of hydroperoxides is half order in rate of initiation. The rates of oxygen uptake, alcohol formation, and aldehyde + ketone formation are intermediate and are assumed to obey a composite relation:

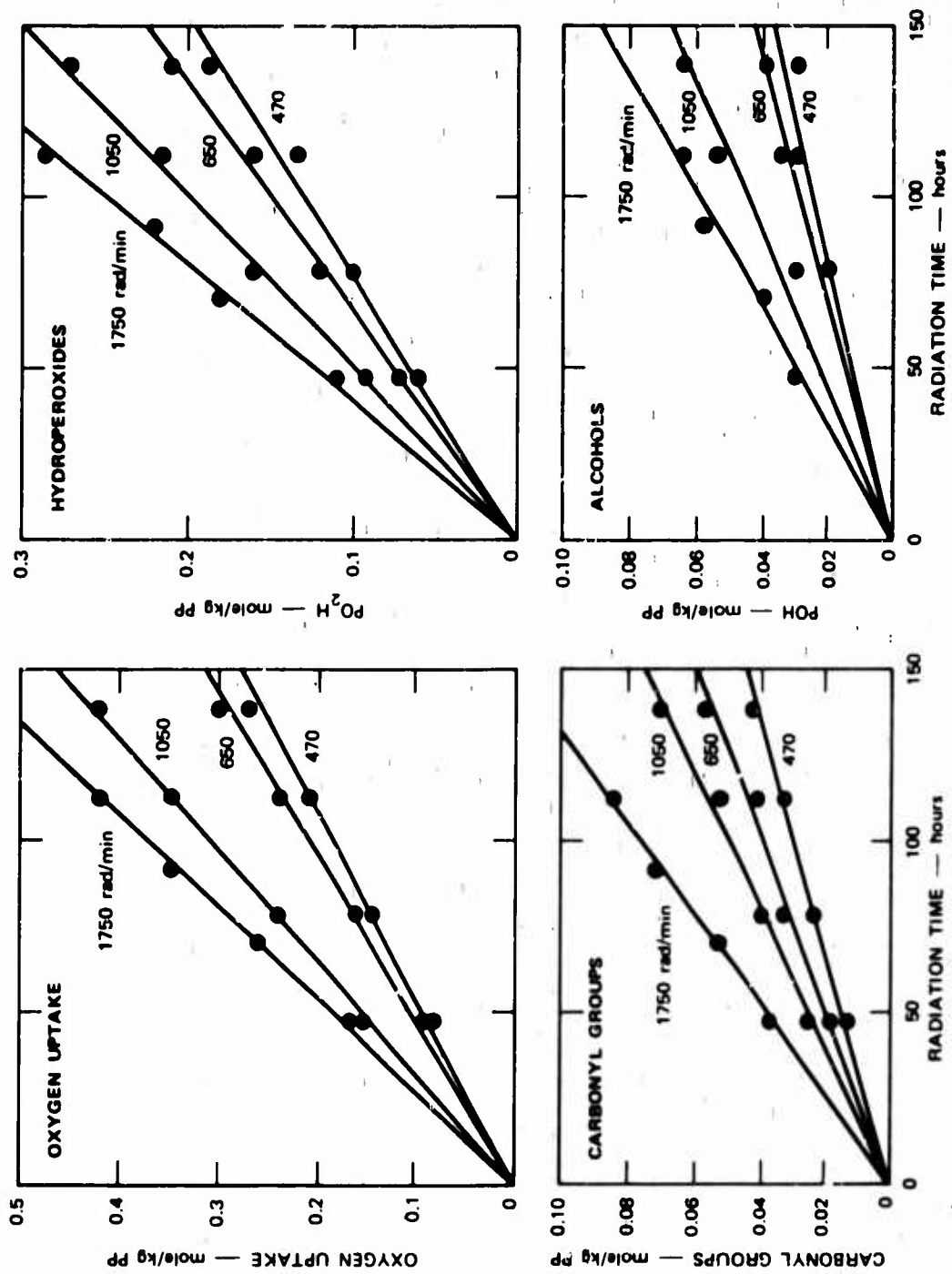
$$R = a I + b I^{\frac{1}{2}} \quad (1)$$

The radiochemical yield G, for oxygen uptake, i.e., the number of molecules of oxygen consumed per 100 eV absorbed, increases from 35 to 63

Table I

γ -INITIATED OXIDATIONS OF PP ($\bar{M}_n = 14,300$) at 22°
(Concentrations are in mole/kg PP)

Dose Rate, rad/min	Time, hr	Dose, Mrad	ΔO_2	PO ₂ H	P ₂ O ₅	>C=O	POH	Acctd. For, %	Net Chain Scission, mole/kg PP
470	47	1.3	0.07 _g	0.06	--	0.01 ₃	--	--	0.003
	78	2.2	0.14 ₅	0.10	--	0.02 ₃	0.02	--	0.006
	112	3.16	0.21	0.13 ₅	0.01	0.03 ₃	0.03	84	0.008
	138	3.9	0.27	0.18 _g	0.01 ₂	0.04 ₃	0.03	88	0.011
650	47	1.83	0.08 _g	0.07	--	0.01 _g	--	--	0.004
	78	3.06	0.15	0.12	0.00 ₇	0.03 ₃	0.02	96	0.007
	112	4.35	0.24	0.16	0.01 ₅	0.04 ₂	0.03 ₅	89	0.008
	138	5.4	0.30	0.21	0.02	0.05 ₇	0.04	93	0.012
1050	47	3.0	0.15 ₃	0.09	0.01 ₁	0.02 ₅	--	--	0.006
	78	4.95	0.24	0.16	0.01 ₄	0.04	0.03	87	0.012
	112	7.05	0.34 ₇	0.21 ₅	0.01 ₉	0.05 ₃	0.05 ₅	83	0.018
	138	8.7	0.42	0.27	0.02 ₅	0.07	0.06 ₅	88	0.019
1750	47	4.95	0.16 ₇	0.11	0.01 ₄	0.03 ₇	0.03	94	0.013
	70	7.35	0.26	0.18	0.02 ₅	0.05 ₃	0.04	97	0.016
	91	9.55	0.34 ₇	0.22	0.03	0.07 ₂	0.06	91	0.023
	112	11.6	0.42	0.28 ₅	0.04	0.08 ₄	0.06 ₅	95	0.024
250,000	0.33	5.2	0.04 _g	0.00 ₇	0.01 _g	0.02 ₅	0.02	95	0.013



TA-8012-10

FIGURE 2 OXIDATION PRODUCTS AS A FUNCTION OF RADIATION TIMES AND DOSE RATES
IN OXIDATIONS OF PP AT 22°C

Table II
RATES OF OXIDATION (R) AND RADIATION YIELDS (G) IN
γ-INITIATED OXIDATIONS OF PP AT 22°
(Rates are in millimoles/kg PP/hr)

Dose Rate, rad/min		470	650	1050	1750	250,000
ΔO ₂	R	1.84	2.1	3.0	3.8	143
	G	63	52	46	35	9.2
ΔI ^a	R	0.31	0.43	0.68	1.15	164
	G	10.4	10.4	10.4	10.5	10.5
PO ₂ H	R	1.32 (71.8) ^b	1.5 (71.1) ^b	2.0 (66.8) ^b	2.5 (65.7) ^b	22 (15.4) ^b
	G	45	37	30.5	23	1.4
P ₂ O ₂	R	0.09 (4.8)	0.12 (5.6)	0.2 (6.7)	0.33 (8.6)	47 (33)
	G	3	2.9	3.1	3	3
>C=O	R	0.29 (8)	0.39 (9.2)	0.51 (9.5)	0.8 (10.4)	75 (26)
	G	0.44 ^c 10	0.46 ^c 9.6	0.56 ^c 7.8	0.61 ^c 7.3	0.92 ^c 4.8
POH	R	0.26 (7)	0.29 (7)	0.46 (7.6)	0.6 (8)	60 (21)
	G	9.0	7.2	7.0	5.5	3.8
Scission	R	0.06 ₈	0.09 ₃	0.14	0.24	39
	G	2.2	2.3	2.1	2.2	2.5
ΔO ₂ calc ^d	R	1.69	1.96	2.68	3.55	136
	G	57.5	48.3	41	32.5	8.7
$\frac{\Delta O_2 \text{ calc}}{\Delta O_2 \text{ obs}}, \%$		91.3	92.8	87.6	95.3	95.4
Kinetic chain length ^e		5.5	4.5	3.9	2.9	0.4
$k_p / (2k_t)^{1/2} \times 10^4$		0.67	0.64	0.71	0.67	1.06

^aΔI = 2 P₂O₂ + that part of >C=O that is first order in dose rate.

^bEach number in parentheses is the % of ΔO₂ accounted for by the indicated product.

^cFraction of >C=O that is first order in dose rate.

^dG_{PO₂H} + G_{P₂O₂} + (G_{POH} + G_{>C=O})/2.

^eNumber of molecules of O₂ consumed in propagation per initiating radical

$$= \frac{G_{O_2} - 5.2}{10.4}$$

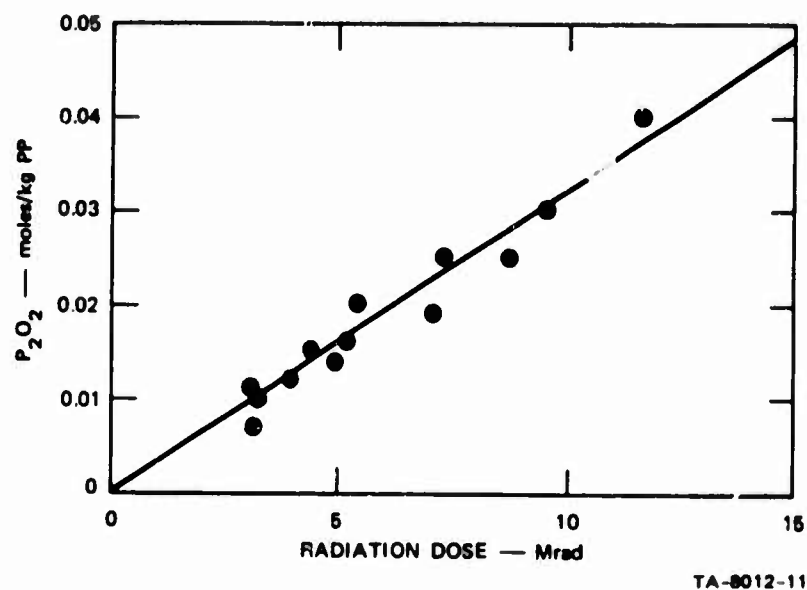


FIGURE 3 FORMATION OF DIALKYL PEROXIDES IN OXIDATIONS OF PP AT 22°

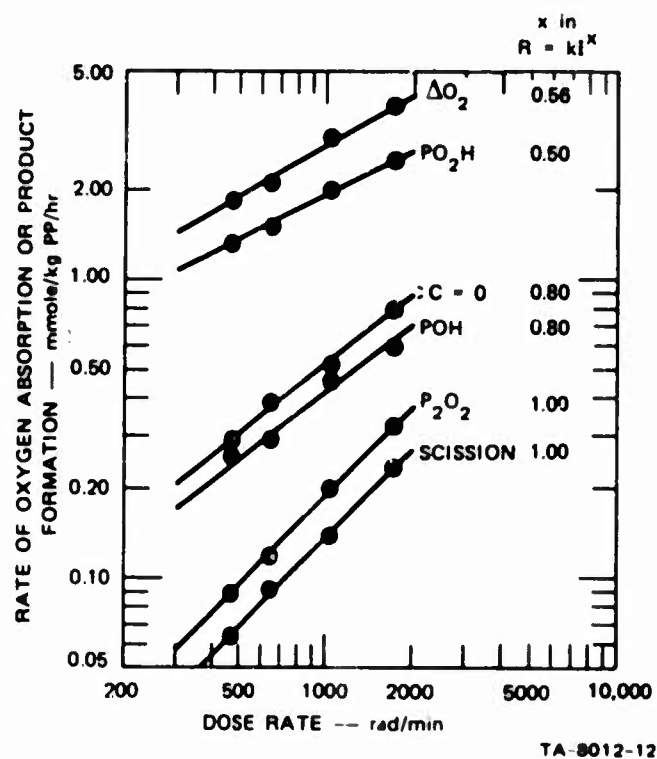


FIGURE 4 RATES OF OXYGEN ABSORPTION OR PRODUCT FORMATION AS A FUNCTION OF INITIATION RATE IN OXIDATIONS OF PP AT 22°

with decreasing rate. These high values of G_{O_2} establish the existence of a chain reaction process. Since $G_{O_2} = K R/I$, the kinetic law can be written as

$$G_{O_2} = \alpha + \beta I^{-1/2} \quad (2)$$

where $\alpha = K_a$ and $\beta = K_b$. Figure 5 shows that plots of G values for ΔO_2 and products against $I^{-1/2}$ are straight lines. The intercepts α are the radiochemical yields of products formed in reactions that are first order in rate of initiation; these reactions are initiation, all cage reactions, termination, and propagation by alkoxy radicals, in or out of the cage. The slopes β are the radiochemical yields of products formed at unit rate of initiation in reactions that are half order in rate of initiation. Thus, $\beta = 0$ for dialkyl peroxides, whereas $\alpha = 0$ for hydroperoxides. Values of α and β for each oxidation product are given in the table in Figure 5. Intercepts α were located accurately by using an electron beam from a 1-MeV resonance transformer and a very high dose rate (250,000 rad/min) to initiate the oxidation. Here the main products are dialkyl peroxides, alcohols, and carbonyl compounds, whereas the amounts of hydroperoxides are very low.

Figure 6 plots the net chain scissions in all our ^{22}O radiation experiments as a function of total dose at all dose rates. This plot confirms that $G_{\text{scissions}} = 2.2$.

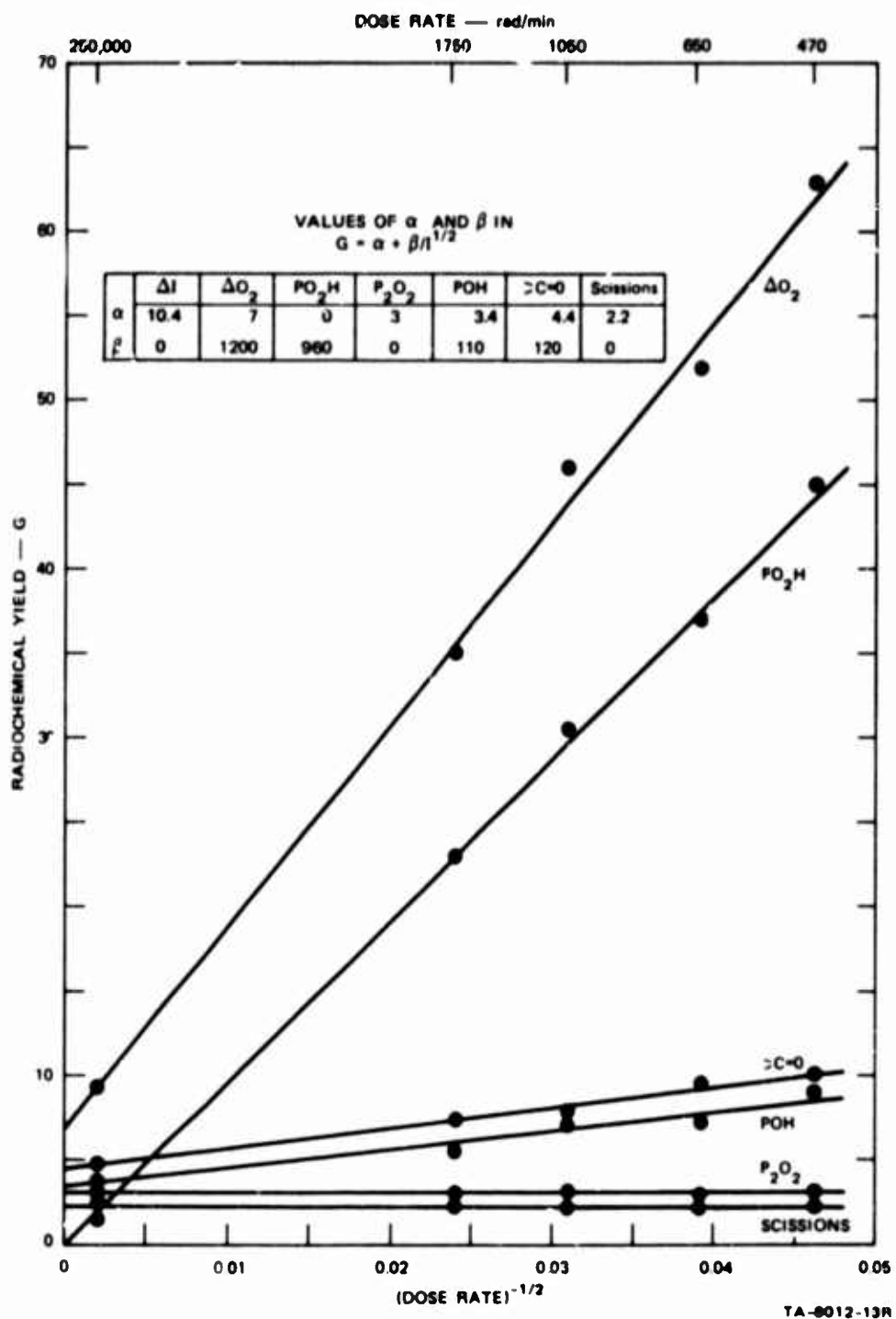


FIGURE 5 RADIOCHEMICAL YIELDS (G) AS A FUNCTION OF (DOSE RATE)^{-1/2} IN OXIDATIONS OF PP AT 22°

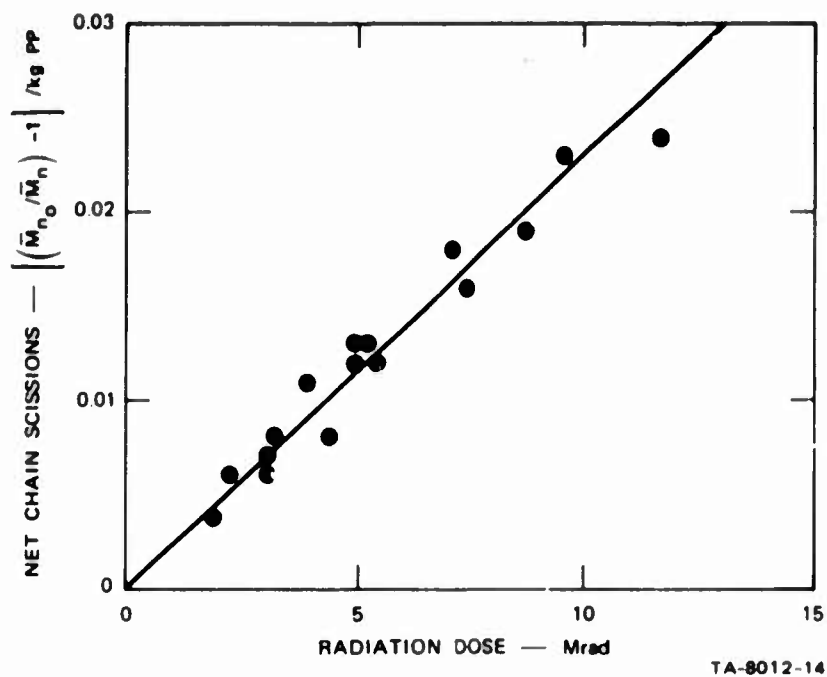
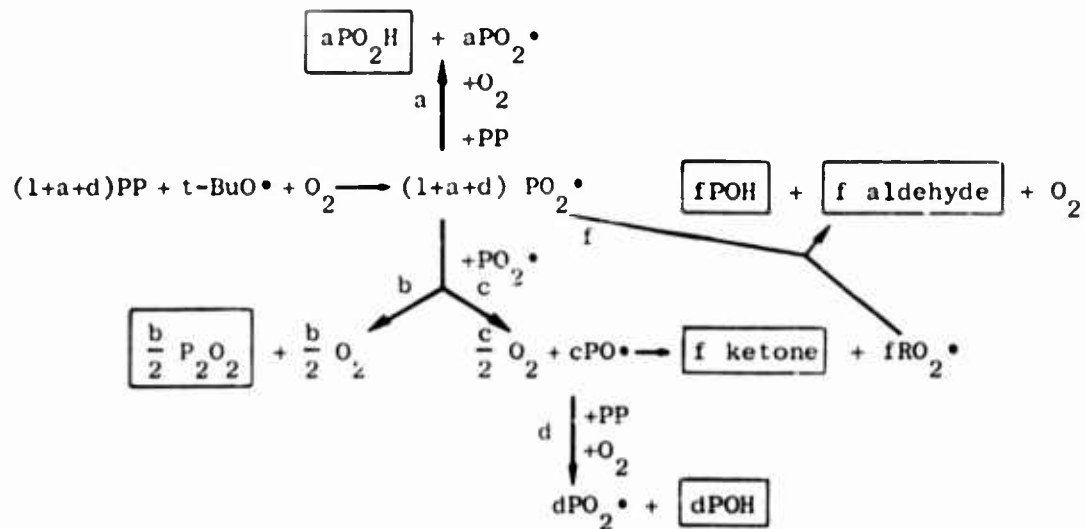


FIGURE 6 NET CHAIN SCISSIONS IN INITIATED OXIDATIONS OF PP AT 22°

4.3. Summary and Conclusions

The data in Tables I and II are now discussed in terms of Equation (2), the values of a and d in Figure 5, and the following reaction scheme:



At very high dose rates, the $8/I^{1/2}$ term can be neglected, and the α values are then the G values for product formation when G_1 for initiating radicals is 10.4.

The last line in Table III shows the material balance, based on α values, for 2.0 initiating radicals for the part of the oxidation that is first order in dose rate. The other equations show how the reactions in the scheme give a perfect calculated fit for the experimental relation. Hydrogen abstraction by $PO\cdot$ radicals, reaction d, provides 0.23 additional $PO_2\cdot$ radicals for each initiating pair. Calculations show that: (1) 64% of the cage interactions of $2PO_2\cdot$ radicals are terminating, (2) 58% of the total terminations come from reactions of $2PO_2\cdot$, and 42% involve primary radicals, (3) 65% of the $PO\cdot$ radicals cleave and result in chain termination, and 35% react with PP to give POH.

Table III

MATERIAL BALANCE FOR FIRST-ORDER
PORTION OF OXIDATION OF PP AT 22°

$2 \text{ PP} \longrightarrow 2 \text{ PP}\cdot + \text{H}_2$
$2 \text{ PP}\cdot + 2 \text{ O}_2 \longrightarrow 2 \text{ PO}_2\cdot$
$1.16 \text{ PO}_2\cdot \longrightarrow 0.58 \text{ P}_2\text{O}_2 + 0.58 \text{ O}_2$
$0.65 \text{ PO}_2\cdot \longrightarrow 0.65 \text{ PO}\cdot + 0.325 \text{ O}_2$
$0.42 \text{ PO}\cdot + 0.42 \text{ O}_2 \longrightarrow 0.42 \text{ RO}_2\cdot + 0.42 \text{ ketone (cleavage)}$
$0.42 \text{ RO}_2\cdot + 0.42 \text{ PO}_2\cdot \longrightarrow 0.42 \text{ aldehyde} + 0.42 \text{ POH} + 0.42 \text{ O}_2$
$0.23 \text{ PO}\cdot + 0.23 \text{ PP} + 0.23 \text{ O}_2 \longrightarrow 0.23 \text{ POH} + 0.23 \text{ PO}_2\cdot$
Calculated: $h\nu + 2.23 \text{ PP} + 1.325 \text{ O}_2 \longrightarrow 0.58 \text{ P}_2\text{O}_2 + 0.42 \text{ ketone} +$ $0.42 \text{ aldehyde} + 0.65 \text{ POH} + \text{H}_2$
Experimental: $h\nu + 2.23 \text{ PP} + 1.345 \text{ O}_2 \longrightarrow 0.577 \text{ P}_2\text{O}_2 + 0.423 \text{ ketone} +$ $0.423 \text{ aldehyde} + 0.654 \text{ POH}$

Although the 0.42 cleavage shown in Table III corresponds exactly to the observed net experimental cleavage, this relation can only be a coincidence requiring explanation. Table III shows that 0.58 P_2O_2 cross-links are formed per initiating pair. To account for 0.42 net cleavage, there must be 0.58 cleavage that we have not yet accounted for. It could arise mostly from C-C cleavages by radiation (part of chain initiation, with $G \leq 3$) and partly from radiolysis of PO_2H to give $>C=O$ compounds and cleavage in the half-order part of the oxidation.

We now consider the β values that measure the oxidation products whose yields are half order in dose rate and that are formed in propagation reactions outside the cage, where termination is statistical, second order in radicals. The β values correspond to the total yields of products at very low rates of initiation where $\beta/I^{1/2} \gg \alpha$. The principal product is POH , which accounts for 80% of the oxygen absorption in this part of the reaction. However, we are unable to see how the minor proportions of $>C=O$ and POH can be formed in a purely half-order reaction. We conclude that the orders of the reactions that produce all the $>C=O$ and POH are complex, between 0.5 and 1.0, and that their resolutions into α and β terms is only a mathematical approximation. The overall formation of $>C=O$ is less than first order in dose rate because more of the primary $RO_2\cdot$ radicals propagate instead of terminating as the dose rate decreases, resulting in production of ketone by cleavage that is not associated with chain termination. We propose that part of the formation of ROH that appears to be half order in dose rate actually arises in secondary reactions, such as decomposition of PO_2H , which accumulates at a rate that is half order in dose rate. About 10% of the half-order oxygen absorption is not accounted for by products, but much of this is in volatile products (Section 4.2).

The discussion above is in terms of two limiting cases, at very high and very low dose rates. Under other conditions, the overall results and the contributions of each limiting case are given by equation (2).

5. γ -INITIATED OXIDATIONS OF PP AT 45°

5.1. Rates and Products of Oxidations of PP at 45°

To determine the influence of temperature on the oxidation of atactic PP and to compare γ and DBPO initiations at 45°, we carried out γ irradiations of the polymer at this temperature. Experimental conditions and analytical methods were the same as those described in Section 4.1 except that the molecular weight of the polymer, \bar{M}_n , was 41,000, to approach those of the ethylene-propylene copolymers.²

Oxidations of PP were carried out for 25, 47, and 75 hours at dose rates of 470, 650, and 1750 rad/min. The oxygen absorptions and oxidation products for each experiment, as shown in Table IV and Figures 7 and 8, increase linearly with the irradiation time and total dose. Thus the rate of oxidation is constant over the whole range of doses investigated.

Table V shows, for the four dose rates studied, the rates of oxygen consumption (R) and formation of oxidation products and the corresponding radiochemical yields (G). The main oxidation product is PO_2H , which accounts for more than 70% of the oxygen uptake, whereas POH , $>\text{C}=\text{O}$, and P_2O_2 account for about 10%, 4%, and 3%, respectively. These oxidation products account for 83% to 92% of the observed oxygen uptakes. The best oxygen balances are for the shortest times and lowest dose rates. The poorer balances with longer reaction times apparently reflect secondary reactions. This material balance is improved if we take into account the volatile products, which represent between 5% and 10% by volume of the oxygen consumption (Sections 4.1, 4.2).

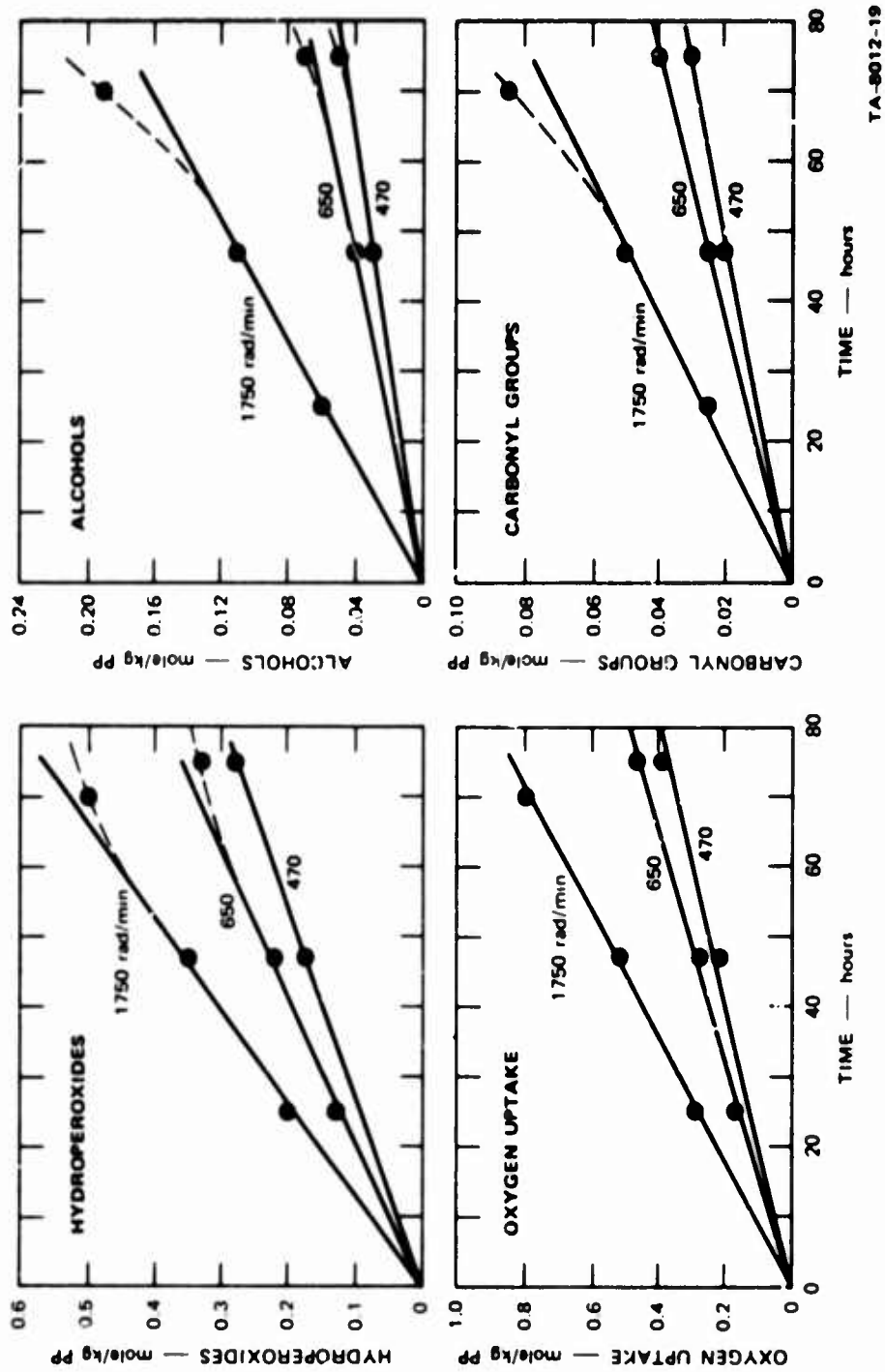
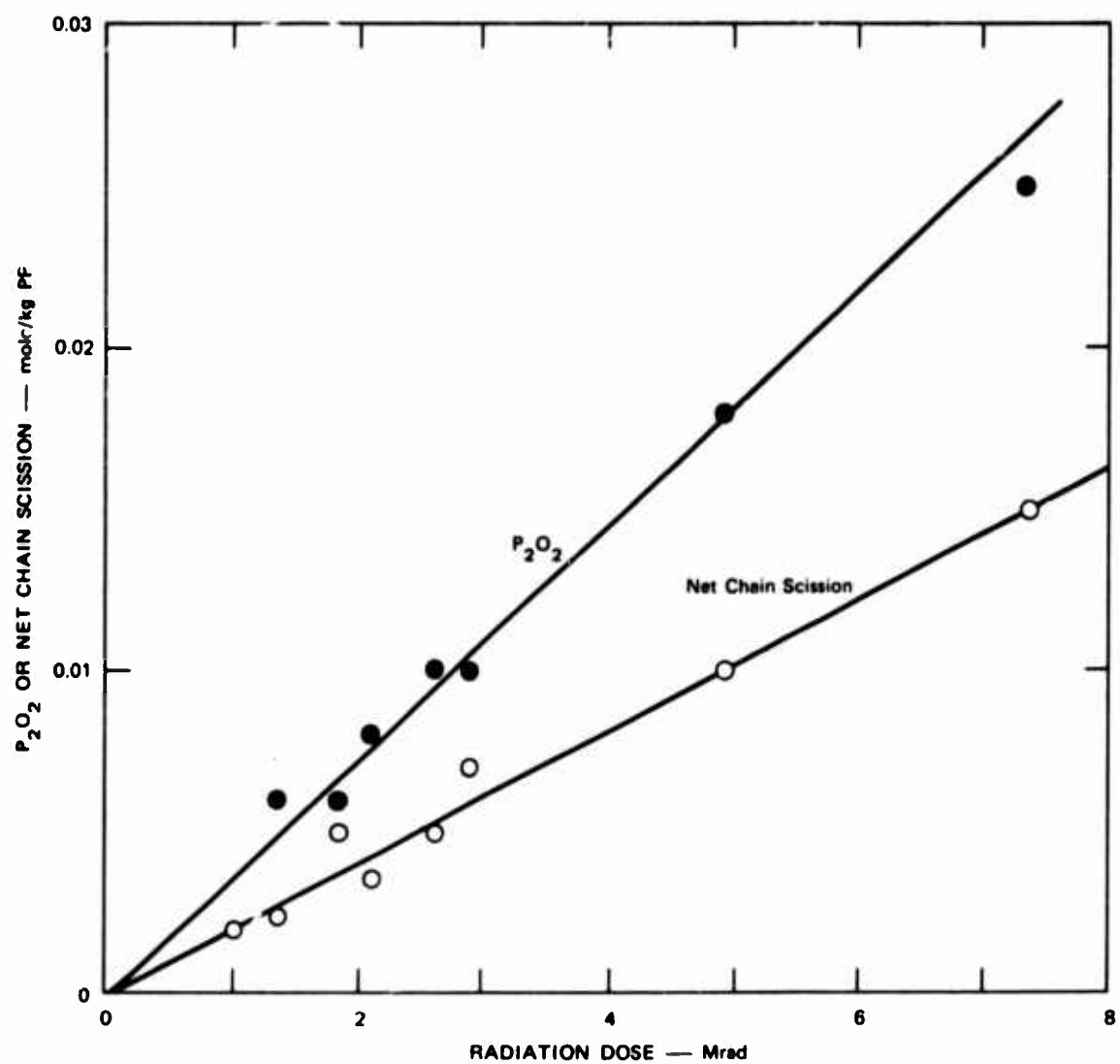


FIGURE 7 γ -INITIATED OXIDATIONS OF PP AT 45°



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FIGURE 8 P_2O_2 AND NET CHAIN SCISSION IN γ -INITIATED OXIDATIONS OF PP AT 45°

Table IV

γ -INITIATED OXIDATIONS OF PP ($\bar{M}_n = 41,000$) AT 45°
(Concentrations are in mole/kg PP)

Dose Rate, rad/min	Time, hr	Dose, Mrad	ΔO_2	PO ₂ H	P ₂ O ₂	>C=O	POH	O ₂ Acctd. For, %	Net Chain Scission, mole/kg PP
470	47	1.33	0.22	0.17	0.006	0.02	0.03	91.2	0.0025
	75	2.1	0.39	0.28	0.008	0.03	0.05	84.1	0.0035
	25	0.98	0.17	0.13	--	--	--	--	0.002
650	47	1.83	0.28	0.22	0.006	0.025	0.04	92.2	0.005
	75	2.9	0.47	0.33	0.011	0.04	0.07	84.5	0.007
	25	2.62	0.29	0.20	0.01	0.025	0.06	87.1	0.005
1,750	47	4.93	0.52	0.35	0.018	0.05	0.11	86.2	0.010
	70	7.35	0.80	0.50	0.029	0.085	0.19	83.3	0.015
250,000	0.5	7.5	0.125	0.047	0.025	0.04	0.055	95.6	--

Table V
RATES OF OXIDATION (R) AND RADIATION YIELDS (G) IN
 γ -INITIATED OXIDATIONS OF PP AT 45°
(Rates are in millimoles/kg PP/hr)

Dose Rate, rad/min		470	650	1750	250,000
ΔO_2	R	5.1	6.3	11.0	250
	G	174	156	101	16.1
ΔI^a	R	0.32	0.44	1.20	171
	G	11.0	11.0	11.0	11.0
PO_2H	R	3.7 (72.8) ^b	4.8 (73.8) ^b	7.6 (69.3) ^b	94 (37.8) ^b
	G	126	119	70	6.0
P_2O_2	R	0.1 (2)	0.14 (2.2)	0.38 (3.4)	50 (20)
	G	3.4	3.5	3.4	3.2
$>C=O$	R	0.41 (4.0)	0.52 (4.1)	1.04 (4.7)	80 (16)
	G	14.0	12.8	9.5	5.1
POH	R	0.64 (6.3)	0.86 (6.8)	2.2 (10.0)	110 (22)
	G	22.0	21.2	20.2	7.0
Scission	R	0.055	0.085	0.22	
	G	1.9	2.1	2.0	
ΔO_2 calc ^c	R	4.33	5.64	9.60	239
	G	148	139.7	88	15.3
$\frac{\Delta O_2 \text{ calc}}{\Delta O_2 \text{ obs}}, \%$		84.8	89.4	87.4	95.6
Kinetic chain length	d	15.3	13.7	8.7	0.95
	e	105	94	61	9.3
$k_p/(2k_t)^{1/2}$ $\times 10^4$	unc.	1.93	2.02	2.1	2.78
	e	4.85	5.05	5.25	7.0

^a $\Delta I = 2 P_2O_2$ + that part of $>C=O$ that is first order in dose rate.

^bEach number in parentheses is the % of ΔO_2 accounted for by the indicated product.

^c $G_{PO_2H} + G_{P_2O_2} + (G_{POH} + G_{>C=O})/2$.

^dNumber of molecules of O_2 consumed in propagation per initiating radical

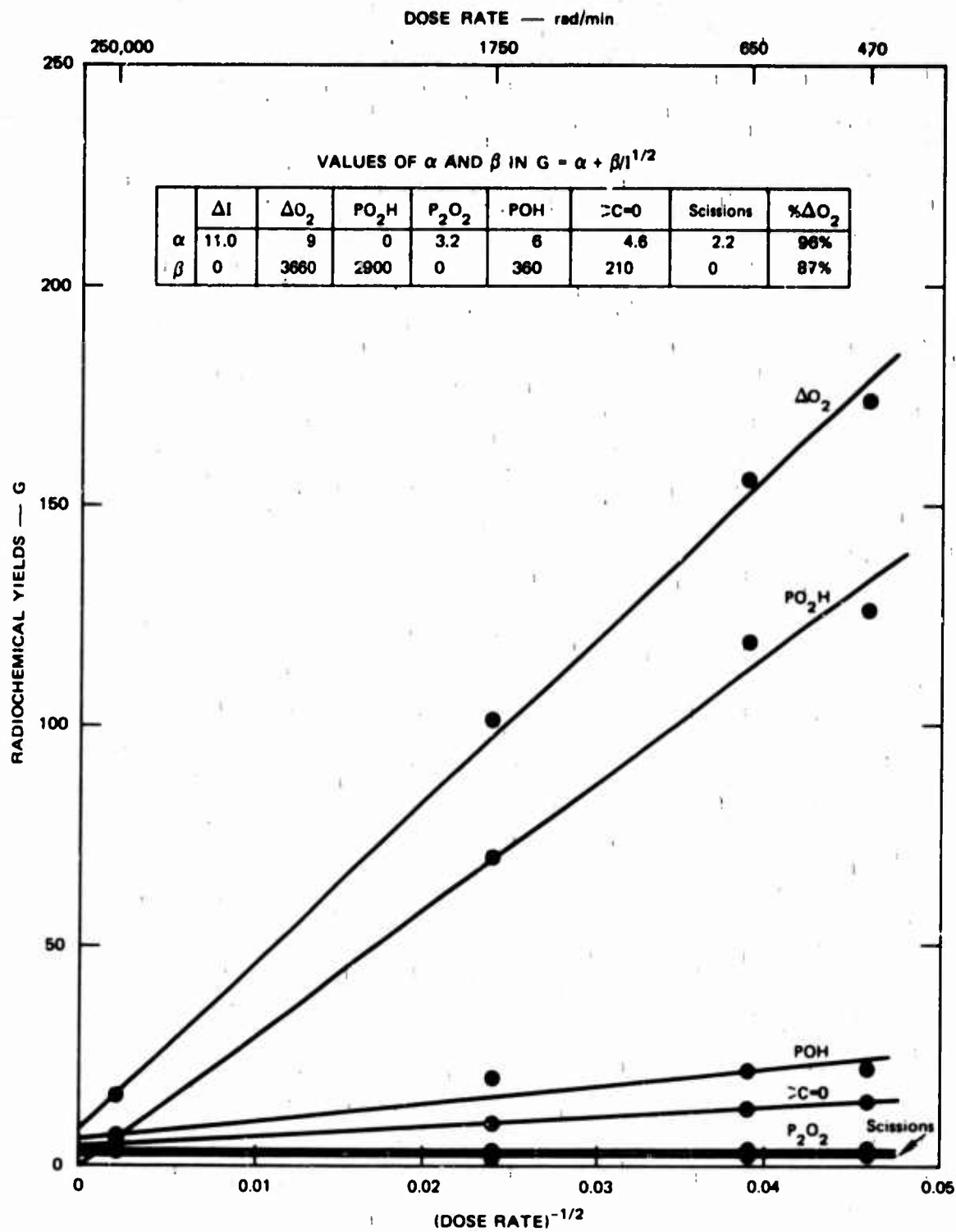
$$= \frac{G_{O_2} - 5.5}{11.0}$$

^eCorrected for 16% escape of $PO_2\cdot$ radicals.

Formation of P_2O_2 and net chain scissions are first order in rate of initiation; the rate of formation of PO_2H is half order in rate of initiation, and the rates of oxygen uptake, POH formation, and $>C=O$ formation are intermediate and are assumed to obey relations (1) and (2) in Section 4.2. Figure 9 shows that plots of G values for ΔO_2 and products against $I^{-\frac{1}{2}}$ are straight lines. The G values also give the intercepts α (radiochemical yields of products formed in reactions that are first order in rate of initiation) and the slopes β (radiochemical yields of products formed at unit rate of initiation in reactions that are half order in rate of initiation). Intercepts α were located accurately by an oxidation carried out at a very high dose rate (250,000 rad/min), using an electron beam. As shown in Figure 8, net chain scissions are a linear function of the irradiation dose, with $G_{\text{scissions}} = 2.0$, about the same value as at 22° .

According to the proposed scheme for the oxidation of PP, the yield of initiating radicals at 45° is $2G_{P_2O_2} + \text{yield of } >C=O$ that is first order in dose rate, i.e., $G_I = 2(3.2) + 4.6 = 11.0$, nearly the same value as at 22° ($G_I = 10.4$). The number of molecules of oxygen consumed in propagation per average initiating radical ($G_{\Delta O_2} - 5.5$)/11.0, decreases from 15.3 to 8.7 with increasing dose rate.

The material balance for the first-order portion (α values) of a PP oxidation at 45° is given in Table VI. Experimentally, we found that 1.63 molecule of oxygen is consumed per initiating radical pair in the first-order portion of ΔO_2 , in good agreement with the calculated value. Calculations show that (1) 51.1% of the interactions of 2 $PO_2\cdot$ radicals are terminating, (2) 58% of the total terminations come from reactions of 2 $PO_2\cdot$, (3) 38.5% of the $PO\cdot$ radicals cleave and result in chain terminations, and 61.5% react with PP to give POH . Hydrogen abstraction by $PO\cdot$ radicals provides 0.67 additional $PO_2\cdot$ radical for each initiating pair.

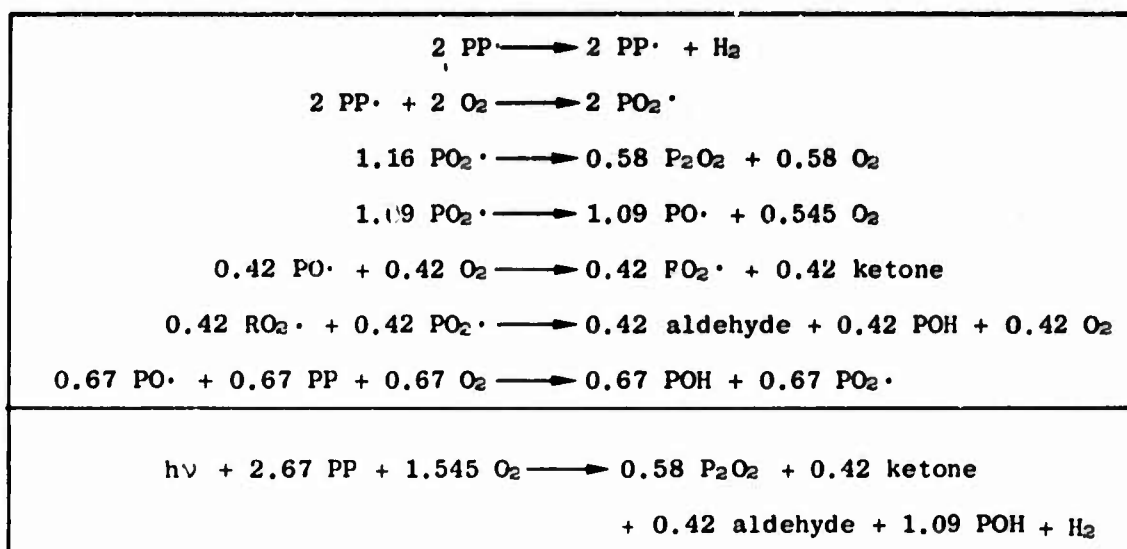


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FIGURE 9 RADIOCHEMICAL YIELD AS A FUNCTION OF (DOSE RATE)^{-1/2} IN γ -INITIATED OXIDATIONS OF PP AT 45°

Table VI

MATERIAL BALANCE FOR FIRST-ORDER PORTION
OF OXIDATION OF PP AT 45°



In the part of the reaction that is half order in initiation rate (β values), the principal product is PO_2H , which accounts for 79% of the oxygen absorbed in propagation. The minor portions of $>\text{C}=\text{O}$ and POH that are found in half-order reactions may arise in propagation by primary PO_2^\cdot radicals and by decomposition of small amounts of PO_2H . About 13% of the half-order oxygen absorption is not accounted for by products, but some of this is in volatile products.

5.2. Comparison of PP Oxidations at 22° and 45°

We now compare our results of the γ -initiated oxidation of PP at 22° (Table II) and at 45° (Table V). As expected, ΔO_2 , PO_2H , POH , and therefore the kinetic chain length and $k_p/(2k_t)^{1/2}$, increase threefold for the increase in temperature at the same rate of initiation, but P_2O_2 , $>\text{C}=\text{O}$, and net chain scissions seem hardly affected by the change in temperature.

The fraction of $\text{PO}_2\cdot$ interactions that terminates (Tables III and VI) decreases with increasing temperature (64% at 22° and 51.5% at 45°) as more pairs of $\text{PO}\cdot$ radicals escape from the polymer cage. The normal effect of increasing temperature is to increase the fraction of $\text{PO}\cdot$ radicals that cleave. We have no satisfactory explanation for the opposite trend that is found in these experiments. The fraction of chain termination involving a primary $\text{RO}_2\cdot$ radical seems not to be affected by the change in temperature.

5.3. Comparison of DBPO- and γ -Initiated Oxidations of Atactic PP at 45°

We now compare our results on DBPO- and γ -initiated oxidations of PP even though the rates and initiation mechanisms are very different. In γ initiation the rate of formation of radicals is constant throughout the oxidation, whereas the decomposition of DBPO gives high initial rates of initiation that decrease exponentially with time. For example, the same amount of oxygen consumption was found after 50 hours of γ irradiation and after only 7 hours with DBPO, the total amount of initiating radicals formed being 0.02 and 0.14 mole/kg PP, respectively.

PO_2H is the major product of PP oxidation and accounts for 50% to 60% of the oxygen uptake with DBPO initiation and about 70% with γ initiation. The average oxygen absorption in propagation per initiating radical is greater in the γ -initiated oxidation (8 to 15) than in the faster DBPO-initiated one (1 to 2).

The competition between the reactions that are first order in rate of initiation seem to be little influenced by the kind of initiation. Roughly half the interactions of 2 $\text{PO}_2\cdot$ radicals are terminating to give P_2O_2 . The remainder of these interactions give t- $\text{PO}\cdot$ radicals. About half of these abstract hydrogen from the polymer to give POH and continuation of the oxidation chains. The rest cleave to primary alkyl, then give alkylperoxy radicals, most of which terminate with $\text{PO}_2\cdot$ radicals.

At low rates of initiation, some of the primary alkylperoxy radicals must propagate before they terminate, with the result that the associated ketone groups do not correspond to chain termination but to chain propagation. Values of the ratio $k_p/(2k_t)^{1/2}$ are rather similar for both initiations and vary from 2×10^{-4} to 2.8×10^{-4} in γ initiation, and 2×10^{-4} to 4×10^{-4} in DBPO initiation. Although our results on DBPO-initiated oxidation give us no information about the proportions of statistical and geminate terminations, we can expect that the fraction of $PO_2\cdot$ radicals that terminate in the cage should be somewhat less than the 84% found in γ -initiated oxidation (Section 6.2) because of the plasticizing effect of the DBPO used.

6. INHIBITED OXIDATIONS OF PP AT 45°

6.1. Rates of Oxidations

To determine the ability of an inhibitor to interfere with cage reactions, we carried out oxidations of PP in the presence of an antioxidant, 2,6-di-t-butyl-p-cresol, abbreviated here to AH. The results show that the antioxidant does not affect cage reactions but scavenges $\text{PO}_2\cdot$ radicals responsible for chain propagation outside the cage. The procedure followed was the same as in the other γ -initiated oxidations except that the polymer and antioxidant were mixed in pentane solutions and then the pentane was removed under vacuum for 3 hours at room temperature.

All experiments were carried out at 45° either for 75 hours at 650 rad/min or for 70 hours at 1750 rad/min. The total radicals produced (ΔI) are 0.033 and 0.084 mole/kg PP, respectively. Table VII shows the results of oxidizing PP in the presence of increasing initial proportions of AH. The rate of formation of $\text{PO}_2\cdot$ radicals (R_1) was shown in Section 5.1 to be 0.44₅ and 1.20 mmole/kg PP/hr at 650 and 1750 rad/min, respectively. The amounts of oxygen reacted (ΔO_2 in Figure 10) decrease rapidly with increasing concentration of antioxidant. With more than 0.12 initial molecule of AH per initiating radical, ΔO_2 becomes constant. The rate of oxygen consumption is then first order in rate of initiation, and the radiochemical yield, G_{O_2} , is constant at 6.9 at 650 rad/min or at 6.8 at 1750 rad/min. Since 1 molecule of antioxidant per 8 radicals formed is sufficient to suppress all propagation, most of the $\text{PO}_2\cdot$ radicals must be destroyed in the cage.

Table VIII and Figure 11 show oxygen uptake as a function of irradiation time at 650 rad/min for a control and for two low concentrations of antioxidant. The rate of oxygen consumption increases with the

Table VII

EFFECT OF ANTIOXIDANT CONCENTRATIONS AND DOSE RATES
ON INHIBITED OXIDATIONS OF PP AT 45°
(Concentrations are in mole/kg PP)

Dose Rate and Time	$[AH]_0$	$[AH]_0/\Delta I$	ΔO_2	PO_2H	P_2O_2	$\bar{\Delta M}_n$	Net Mole Scission kg PP
650 rad/min for 75 hr, $\Delta I =$ 0.033 $\frac{\text{mole}}{\text{kg PP}}$	0 0.0001 0.002 0.004 0.007 ₃ 0.014 ₆ 0.033 0.40	0 0.03 0.06 0.12 0.22 0.44 1.0 12.1	0.47 0.27 ₅ 0.15 0.03 0.02 ₄ 0.02 ₃ 0.02 ₁ 0.02 ₀	0.33 (71) ^a 0.19 (69) 0.10 (67) 0.01 ₂ (40) 0.00 ₃ (12) 0.00 ₂ (9) 0.00 ₂ (9)	0.01 ₁ (2) ^a 0.01 ₂ (4) 0.01 ₃ (9) 0.01 ₅ (50) 0.01 ₅ (62) 0.01 ₄ (61) 0.01 ₅ (72)	-9100 -5200 -1500 + 600 +2000 +2300 +1800	0.007 0.0038 0.001
1750 rad/min for 70 hr, $\Delta I =$ 0.084 $\frac{\text{mole}}{\text{kg PP}}$	0 0.002 ₅ 0.005 ₂ 0.010 ₅ 0.021 0.040 ₅ 0.081 1.01	0 0.03 0.06 ₂ 0.12 ₅ 0.25 0.48 0.97 12.0	0.80 0.56 0.22 0.05 0.05 ₃ 0.05 ₁ 0.05 ₂ 0.05	0.50 (62.5) 0.35 (63) 0.12 (55) 0.01 ₃ (29) 0.00 ₄ (13) 0.00 ₅ (10) 0.00 ₆ (11)	0.02 ₃ (4) 0.03 ₂ (6) 0.03 ₅ (16) 0.03 ₈ (60) 0.03 ₈ (72) 0.03 ₈ (75) 0.03 ₃ (75)	-15500 -8800 -4300 -1400 + 800 +1700 +1200	0.015 0.007 0.003 0.001

^a Each number in parentheses is the percent of ΔO_2 accounted for by the indicated product.

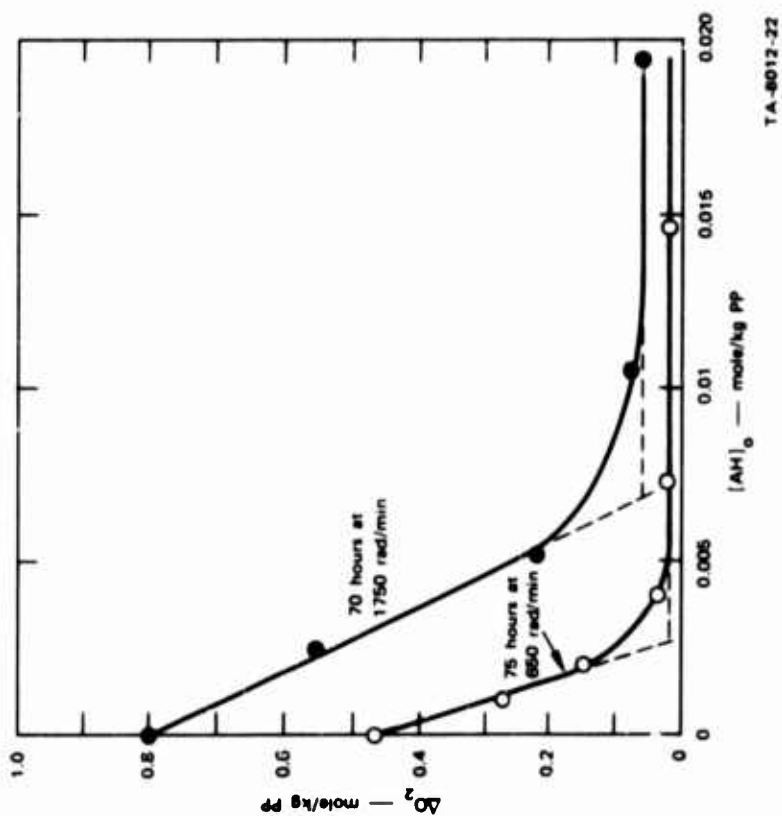


FIGURE 10 DEPENDENCE OF OXYGEN UPTAKE ON INITIAL ANTIOXIDANT CONCENTRATION IN INHIBITED OXIDATIONS OF PP AT 45°

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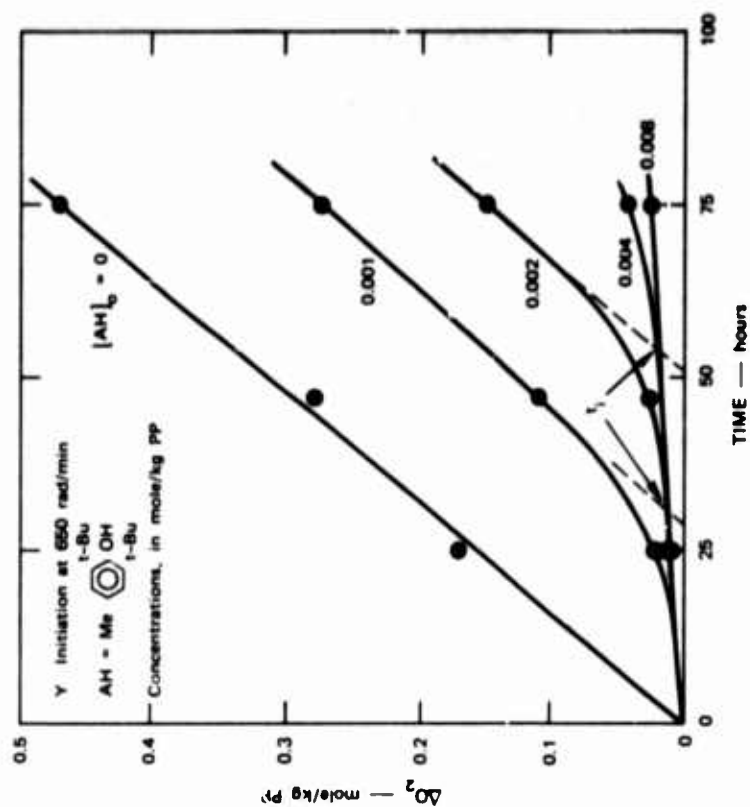


FIGURE 11 O_2 ABSORPTION BY INHIBITED-OXIDATION OF PP AT 45° AS A FUNCTION OF TIME

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Table VIII

INHIBITED OXIDATIONS OF PP AT 45°

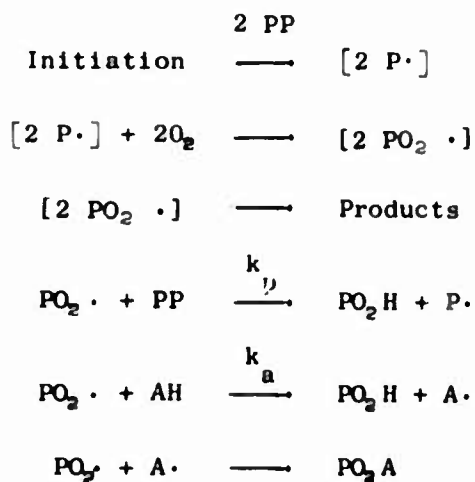
(Dose rate = 650 rad/min; $R_1 = 0.44_8$ mmole/kg PP/hr)

$[AH]_0$ mmole/kg PP	ΔO_2 , mole/kg PP			Time t_1 , ^a hr	$r_1 = 2[AH]_0/t_1$ mmole/kg PP/hr	r_1/R_1
	25 hr	47 hr	75 hr			
0	0.17	0.28	0.47	0		
1.05	0.02	0.11 ₂	0.27 ₅	30.5	0.06 ₈	0.153
2.00	0.01	0.02 ₅	0.15	54	0.07 ₄	0.166

^a Time t_1 during which $(\Delta O_2)_{\text{propagation}} = 0$.

irradiation time until it reaches, at exhaustion of the antioxidant, the value observed in uninhibited oxidations.

The scheme for inhibited oxidation by 2,6-di-t-butyl-p-cresol can be represented by:



According to this mechanism, all chains terminate either in the cage or with antioxidant, and the rate of oxygen uptake is:

$$-\frac{d[O_2]}{dt} = \frac{R_i + r_1}{2} + r_1 \left(\frac{k_p [PH]}{k_a [AH]} \right) \quad (3)$$

where R_i the total rate of formation of $P\cdot$ radicals and r_1 is the effective rate of formation of free radicals, i.e., the rate at which $PO_2\cdot$ radicals escape from the original caged pair and can undergo chain propagation. When one molecule of antioxidant terminates 2 $PO_2\cdot$ radicals, this leads to the differential equation

$$-\frac{d[AH]}{dt} = \frac{r_1}{2}$$

During the induction period $[AH]_t = [AH]_0 - \frac{r_1 t}{2}$ where $[AH]_0$ is the initial concentration of antioxidant.

6.2. Caged and Free $PO_2\cdot$ Radicals

The rate of formation of free $PO_2\cdot$ radicals may be estimated in two ways: (1) By plotting oxygen consumption as a function of irradiation time at each initial concentration of antioxidant. Extrapolation of the linear, steeply sloping portion of each curve (Figure 11) gives the inhibition period t_1 during which there would be no propagation if there were no transition period between inhibited and normal oxidations. At the time t_1 , $[AH] = [AH]_0 - r_1 t_1 / 2 = 0$, and the initiation rate, $r_1 = 2[AH]_0 / t_1$, can be determined. Table VIII shows that r_1 is about 0.07 mmole/kg PP/hr, which corresponds to an average ratio r_1 / R_i of 16%. (2) By plotting oxygen consumption as a function of the initial concentration of antioxidant at a given irradiation time. When all the

antioxidant has been consumed, i.e., at lowest $[AH]_0$, the oxygen uptake after 75 hours of irradiation is: $\Delta O_2 = (75 - t_1)(d[O_2]/dt)_{[AH]_0 = 0}$. Since $t_1 = 2[AH]_0/r_1$, ΔO_2 decreases linearly with increasing initial concentrations of antioxidant (Figure 10). The extrapolation of this straight line to the horizontal one corresponding to ΔO_2 with excess of $[AH]$ gives the critical concentration of antioxidant $[AH]_c$ necessary to prevent all chain propagation in 75 hours at 650 rad/min if there were no transition stage: $[AH]_c = (r_1 \times 75)/2$. Table IX shows the values of r_1/R_1 obtained by this method at both dose rates, again about 16%.

Table IX

CALCULATION OF THE EFFECTIVE RATES OF INITIATION
(Concentrations are in mmole/kg PP;
rates are in mmole/kg PP/hr)

Dose Rate, rad/min	Time t, hr	R_1	$[AH]_c^a$	$r_1 = \frac{2[AH]_0}{t}$	r_1/R_1
650	75	0.445	2.6	0.069	15.5
1,750	70	1.20	6.8	0.194	16.2

a Lowest initial concentration of antioxidant for which
(ΔO_2) propagation = 0.

According to these results, 16% of all the $PO_2 \cdot$ radicals formed escape from the cage to undergo propagation and statistical termination, and the remaining 84% disappear by geminate terminations in the cage. Consequently, the true kinetic chain length for propagation in neat polypropylene is six times that previously calculated and varies between 60 and 100 over the range of dose rates studied (Table V). When the

concentration of antioxidant is sufficient to inhibit all propagation, G for oxygen uptake is

$$G_{O_2} = 0.84(G_R)/2 + 0.16 G_R.$$

As the yield of initiating radicals $G_R = 11.0$, $G_{\Delta O_2} = 6.4$, in good agreement with the observed yield of ΔO_2 at the two dose rates, 6.8 and 6.9.

6.3. Calculation of k_a/k_p

The ratio k_a/k_p can be calculated by integration of equation (3) between time 0 and t :

$$-(\Delta O_2)_t = \frac{\Delta I + \Delta r_1}{2} + \Delta r_1 \left(\frac{k_p [PH]}{k_a [AH]} \right)$$

where

$$[AH] = \frac{[AH]_0 + [AH]_t}{2} = [AH]_0 - \frac{\Delta r_1}{4}$$

Table X shows that the ratio k_a/k_p is 4700 ± 500 .

6.4. Changes in Molecular Weight

As shown in the last column of Table VII, net chain scissions decrease with increasing concentrations of antioxidant. When all propagation is suppressed, i.e., for $[AH]_0/\Delta I > 0.12$, the molecular weight of PP is only slightly higher than before irradiation, even though peroxide

Table X

CALCULATION OF k_p

(Concentrations in mmole/kg PP;

[PP] = 23.8 mole/kg; rates in mmole/kg PP/hr)

Dose Rate, R_i, r_i	Time, hr	$[AH]_0$	ΔI	Δr_i	ΔO_2	k_a/k_p^a
650 rad/min $R_i = 0.445$ $r_i = 0.07$	25	1.05	11.1	1.7 ₅	20	5,000
	25	2.0	11.1	1.7	11	5,800
	47	2.0	21.0	3.3	25	5,150
	75	4.0	33.4	5.2 ₅	30	4,350
	75	7.3	33.4	5.2 ₅	24	4,500
1,750 rad/min $R_i = 1.2$ $r_i = 0.19_4$	75	10.5	84	13.6	60	4,150
	75	21	84	13.6	53	4,600
	75	40.5	84	13.6	51	4,400

$$^a k_a/k_p = \frac{[PP]\Delta r_i[PP]}{\left(-\Delta O_2 - \frac{\Delta I_i + \Delta r_i}{2}\right)\left([AH]_0 - \frac{\Delta r_i}{4}\right)}$$

crosslinking has occurred. This result is in agreement with our previous observation on the net cleavage in the oxidation of PP at 22° (section 4.3). It can be explained either by intramolecular crosslinking or by radiation-induced C-C cleavages, which offset intermolecular crosslinking.

7. OXIDATIONS OF PP IN HEXANE SOLUTION

This section includes all our work with hexane as solvent, even though some experiments use DBPO instead of γ initiation. All experiments were carried out with atactic PP of $\bar{M}_n = 41,000$. The general conclusion is that rates of oxidation of PP, per kg PP per initiating

radical, are similar in bulk and in solution. The substantial loss of initiating $\text{PO}_2\cdot$ radical pairs in cage termination in bulk is offset by larger values of $k_p/(2k_t)^{1/2}$ in bulk. This compensation is similar to the different compensation of efficiency of initiation by $t\text{-BuO}\cdot$ radicals and $k_p/(2k_t)^{1/2}$ with changing molecular weight of bulk PP described in Section 5.5 of Reference (1).

7.1. γ -Initiated Oxidations of PP in Hexane at 45°

Oxidations of PP were carried out in solution to determine the effect of decreased viscosity on the oxidation process. Hexane solutions of PP at concentrations of 10 and 22.6 g/100 ml were irradiated for 70 hours at 45° at two dose rates under an initial oxygen pressure (at 25°) of 650 torr. To determine what portion of the oxygen was consumed by oxidation of the solvent, we also carried out γ -initiated oxidations of pure hexane under the same conditions. Table XI shows that hydroperoxides, dialkyl peroxides, and carbonyl compounds are the main oxidation products of hexane and account for 87.5% of the oxygen consumed. Oxidation chains are very short at this temperature, as shown by the small increase of G_{O_2} with decreasing dose rate, 5.2 and 6.0 at 1750 and 650 rad/min, respectively. The extrapolated value α_{O_2} is 3.9, in good agreement with the yield of alkyl radicals in hexane, $G_R = 7.6^{18}$.

Table XI compares the results of four oxidations of PP in solution with oxidations of n-hexane and with previous results for bulk PP (Table IV). The stated amounts of oxygen absorbed by the polymer alone assume that the rates of oxidation of hexane (per kg hexane) in solution are the same as in pure hexane. Values of ΔO_2 in mole/kg PP are about the same for the two concentrations studied and about three-quarters of those found in the oxidation of bulk PP.

(18) E. N. Weber, P. F. Forsyth, and R. H. Schuler, Radiat. Res., 3, 68 (1955).

Table XI
 γ -INITIATED OXIDATIONS OF PP, HEXANE, AND THEIR MIXTURES FOR 70 HOURS AT 45°

	PP Only (Table IV)		Hexane		PP in Hexane				
rate, rad/min	650	1750	650	1750	650	1750	650	1750	1750 ^a
g	350	374	0	0	351	350	300	301	300
Hexane, ml ^b	0	0	5.0	5.0	3.1	3.1	1.0	1.0	1.0
PP, g/liter	900	900			100	100	226	226	226
PP, wt%	100	100			14.6	14.6	31.2	31.2	31.2
ΔO_2 , mole/kg soln.					0.066	0.122	0.114	0.21	0.174
mole/kg PP	0.44	0.90			0.35 ^c	0.60 ^c	0.33 ^c	0.58 ^c	0.47 ^c
mole/kg hexane			0.017	0.040	0.017	0.040	0.017	0.040	0.040
PO_3H , mole/kg soln.					0.047	0.075	0.090	0.138	
mole/kg PP	0.33	0.50			0.28	0.43	0.27	0.41	0.38
mole/kg hexane			0.008 ₅	0.016	0.007 ₆	0.015	0.008	0.016	
P_2O_5 , mole/kg PP	0.01	0.029			0.007	0.02	0.008	0.022	
mole/kg hexane			0.005 ₂	0.012	0.005	0.011			
>C=O , mole/kg	0.037	0.085	d	0.014	0.05	0.10	0.04	0.09	
POH, mole/kg	0.06	0.19	d	d	0.06	0.17	0.05	0.018	
O_2 found, mole/kg	0.39	0.67	0.014	0.035	0.34	0.58	0.32	0.57	
%	89	84	80	87	98	97	98	97.5	
ΔI , mole/kg	0.0045 ^{e,f}	0.0134 ^{e,f}	0.022 ^{g,h}	0.060 ^{g,h}	0.023 ^h	0.064 ^{g,h}	0.025 ^h	0.067 ^h	
					0.031 ^f	0.084 ^f	0.031 ^f	0.084 ^f	
KCL ⁱ	94	61	0.25	0.15	10.8	6.6	10.2	6.4	

^a0.961 g solution contained 0.6₆ mg 2,6-di-t-butyl-p-cresol.

^bDensity of hexane, 0.661 g/ml

^cDetermined by difference between values for solution and solvent.

^dNo measurable amount of group.

^eCorrected for 16% escape from the cage.

^f ΔI in mole/kg PP (Table V).

^gCalculated for G_R in hexane = 7.8.

^h ΔI in mole/kg soln.

ⁱKinetic chain length = $(\Delta O_2 - \Delta I/2)/\Delta I$.

The amounts of hydroperoxides were determined by the Hiatt method, both in the irradiated solution and in the polymer after removal of hexane and hexyl hydroperoxide at room temperature and 10^{-4} torr for four hours. Hexyl hydroperoxides and dihexyl peroxides were determined in the recovered solvent (95% recovery) and found to be about 90% of those in the oxidation of pure hexane. This result supports our conclusion that the rates and products of the cooxidation of hexane have little net effect on the oxidation of dissolved PP and vice versa. Apparently more chain initiation in solution is offset by faster termination in solution.

As shown in Figure 12, the oxygen uptake increases linearly with increasing concentration of polymer when ΔO_2 is expressed in mole/kg solution and [APP] in g/liter. Thus, over a range of concentrations, the oxidation of PP in hexane behaves like an ideal cooxidation. If the concentration is expressed in "wt %", the curve falls below the straight line.

One experiment on the inhibited oxidation of PP in hexane at 1750 rad/min for 70 hours shows that with 0.01 mole 2-6-di-butyl-p-cresol per kg PP ($[AH]_0/\Delta I = 0.125$, which was sufficient to suppress all propagation during the oxidation of bulk PP in Section 6), the oxygen uptake is still about 80% of that without inhibitor. Thus, in solution most of the polymer peroxy radicals produced by initiation are available for propagation reactions (with little or no cage effect), and the kinetic chain lengths are then 6.6 and 10.5 for 1750 and 650 rad/min, respectively, compared with corrected values of 61 and 94 in the oxidation of PP in bulk.

This ten-fold decrease in kinetic chain length can be explained as follows: In the solid state, isolated $PO_2\cdot$ radicals have only a very low mobility and the termination reaction is very slow, as shown by our esr experiments (Section 7 in Reference 1), and the propagation is less affected, proceeding mainly by intramolecular attack to give adjacent hydroperoxide groups. However, in solution, the polymeric $PO_2\cdot$ radicals

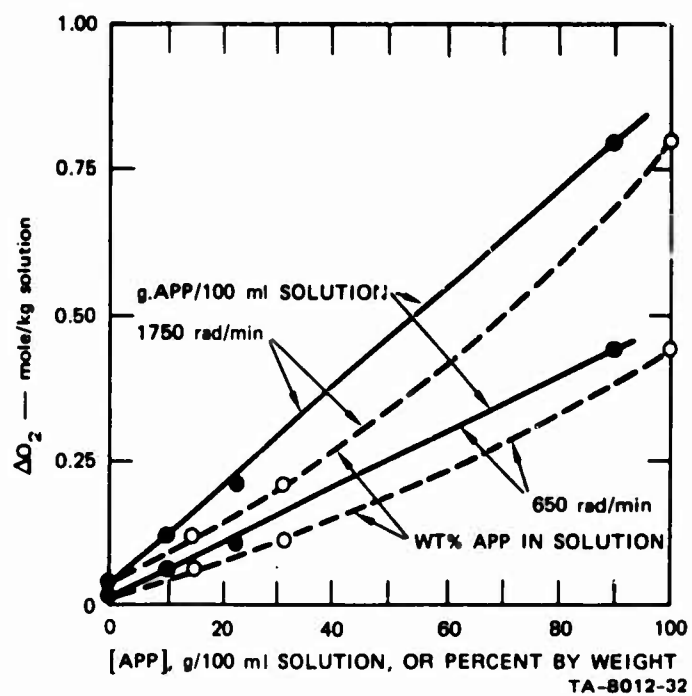


FIGURE 12 DEPENDENCE OF ΔO_2 ON THE CONCENTRATION OF APP IN γ -INITIATED OXIDATIONS IN HEXANE SOLUTIONS

can move freely enough that both k_p and k_t are much higher, but the increase of k_t is greater than that of k_p ; thus, the kinetic chain length in solution is shorter than in bulk.

7.2. DBPO-Initiated Oxidations of PP in Hexane

Results of two sets of experiments in DBPO-initiated oxidations of PP and hexane and their mixtures are summarized in Tables XII and XIII.

An esr study of oxidations of PP and hexane at 58° was carried out to determine the effect of decreased solution viscosity on concentrations of $PO_2\cdot$ radicals. As shown in Table XII, this concentration is about 10^{-5} M, one-hundredth of that in bulk. For an assumed 90% efficiency of initiation,¹⁹ the termination rate constant is calculated to be 1×10^{-6} /M sec in solution, nearly the same as for sec-heptylperoxy radicals in heptane²⁰ at 30°, 2×10^{-6} /M sec. Thus the effects of both bulk viscosity and slow termination constant for tertiary $\Delta O_2\cdot$ radicals have disappeared in hexane solution.

Table XIII shows how $\Delta O_2/\Delta I$ is about the same (4 to 5) for bulk PP and for its 14 and 31 wt% solutions in hexane at 45°. However, for the $PO_2\cdot$ radicals that escape from the initiating cage $\Delta O_2/\Delta I$ is about six times as large.

(19) R. Hiatt and T. G. Traylor, J. Amer. Chem. Soc., 87, 16 (1965). In n-pentane at 45°, the efficiency of free radical production is about 96% (4% yield of t-Bu₂O₂).

(20) J. E. Bennett, D. M. Brown, and B. Mile, Trans. Faraday Soc., 66, 386 (1970).

Table XII
DBPO-INITIATED OXIDATIONS OF PP AND HEXANE AT 58°

	Bulk	Hexane Solution	Calc. for Heptane Only ²⁰
PP, g/liter	900	100	0
DBPO	0.84 mole/kg PP	0.08 M	0.08 M
Efficiency, %	0.3	0.9	0.9
[PO ₂ ·] after 2 min	10 ⁻³ mole/kg PP	10 ⁻⁵ M	0.8 x 10 ⁻⁵ M
k _t , M ⁻¹ sec ⁻¹	340	1 x 10 ⁶	2 x 10 ⁶

Table XIII
DBPO-INITIATED OXIDATIONS OF PP AND HEXANE FOR 7 HOURS AT 45°

Expt. No.	28 (Ref. 1)	82	83
APP, mg	Bulk	300	301
Hexane, ml		1.0	2.8
Hexane, mg		661	1850
DBPO, mg		9.0	11.0
DBPO, μmole		38	47
DBPO, mole/kg PP	0.317	0.127	0.156
DBPO, mole/kg soln.		0.04	0.022
Efficiency, %	0.1	90 (est.)	90 (est.)
ΔI, mole/kg soln.	0.039 ^a , 0.0062 ^b	0.072	0.040
ΔO ₂ , μmole		344	395
ΔO ₂ , mole/kg soln.	0.153 ^a	0.36	0.184
ΔO ₂ /ΔI	3.9, 25 ^b	4.5	4.6

^a Mole/kg PP.

^b Corrected for 16% escape of PO₂· radicals from cage.

8. **ACKNOWLEDGMENTS**

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